

600 g of a catalyst comprising 2% by weight of RuO₂ on aluminum oxide support particles were installed in a tube reactor having a diameter of 4 cm and fluidized at 340°C by means of 200 standard l/h of HCl and 100 standard l/h of O₂. The HCl conversion was determined at regular time intervals. As the period of operation increased, ever smaller conversions were determined, indicating that the catalyst became deactivated.

Experiment 2

2 g of catalyst were supplied in an isothermally operated fixed bed at (a) 300°C or (b) 340°C with an HCl/O₂ mixture having a molar ratio of HCl : O₂ of 2:1. The HCl conversion was determined in each case.

At the same time, the HCl conversion was calculated by means of the equation shown below under the assumption of ideal flow through the fixed catalyst bed (plug flow). The reaction rate r indicates the number of mole of HCl reacted per second and g of catalyst.

$$r = k_{\text{hin}}^0 \exp\left(-\frac{E_{\text{act}}}{RT}\right) \frac{y_{\text{HCl}} y_{\text{O}_2} (1 + K_{\text{N}_2} y_{\text{N}_2}^2)}{\left(1 + \exp\left(\frac{\lambda}{T}\right) (K_{\text{Cl}_2} y_{\text{Cl}_2} + K_{\text{H}_2\text{O}} y_{\text{H}_2\text{O}})\right)^2} \left(1 - \frac{p^{*0.25}}{K_p^{0.25}} \frac{P_{\text{H}_2\text{O}}^{0.5} P_{\text{Cl}_2}^{0.5}}{P_{\text{HCl}} P_{\text{O}_2}^{0.25}}\right)$$

In this equation:

Parameter	Symbol	Value	Std. dev.	Unit
Particle density	ρ_{particle}	2300		kg/m ³
Empty volume fraction of the bed	ε	0.36		
Reaction rate	r			mol/(kg _{cat} s)
Collision factor	K_{hin}^0	8.00154×10^6	$\pm 8.20653 \cdot 10^5$	mol/(kg _{cat} s)
Activation energy	E_{act}	1.03490×10^5		J/mol
Absolute temperature	T			K
Gas constant	R	8.314		J/mol/K
Mole fraction of component j	y_i			mol/mol
Adsorption constant for chlorine	K_{Cl_2}	0.01117		
Adsorption constant for water	$K_{\text{H}_2\text{O}}$	0.06356		
Adsorption constant for nitrogen	K_{N_2}	7.9255		
Temperature dependence of the adsorption constant		λ 2414		K
Partial pressure of component j	p_i			bar
Equilibrium constant	K_p			
Reference pressure	p^*	1.013		bar

It could be estimated in this way that it is not possible to operate the catalyst

isothermally at 340°C in an industrial fixed bed (catalyst tubes having a diameter of 2 cm). This is because the reaction rate is then so high in the initial region of the catalyst tubes that a hot spot is formed and the catalyst undergoes severe sintering there.

On the other hand, the reaction rate at 300°C is so low that the catalyst can be operated isothermally in an industrial fixed bed.

Experiment 3

The three process variants (1), (2) and (3) described below were studied:

(1) 1.2 kg of catalyst are operated in a fluidized bed and supplied with 100 l/h of HCl and 50 l/h of O₂ at 340°C.

(2) 1.2 kg of catalyst are operated isothermally at 300°C in a fixed bed and supplied with 100 l/h of HCl and 50 l/h of O₂.

(3) 0.6 kg of catalyst are operated at 340°C in a fluidized bed. The fluidized-bed stage is followed by a fixed-bed stage in which 0.6 kg of catalyst are operated isothermally at 300°C.

The conversions achieved in the fluidized-bed reactor were determined experimentally. The conversions achieved in the fixed bed were calculated with the aid of the calculated reaction rate r under the assumption of ideal flow (plug flow).

The conversions determined are shown in the table below for a period of operation of 1 week, 2 months and 1 year.

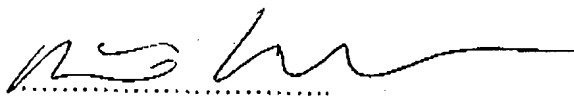
HCl conversion	After 1 week	After 2 months	After 1 year	After replacement of the catalyst in the fluidized bed
(1)	78%	71%	63%	-
(2)	59%	59%	59%	-
(3) after fluidized-bed stage	66%	58%	50%	66%
(4) after fixed-bed stage	75%	69%	63%	75%

Result:

The combination (3) of a fluidized-bed stage at 340°C and a fixed-bed stage at 300°C gives higher HCl conversions than a pure fixed-bed stage (2) at 300°C. Even after one year, the same conversion is achieved by means of the combination (3) as when a pure fluidized-bed stage (1) is used. The advantage of the combination (3) over purely fluidized-bed operation (1) is that only half of the catalyst has to be replaced since only the catalyst of the fluidized-bed stage becomes deactivated. The other half of the catalyst in the fixed-bed stage does not become deactivated. The combination (3) therefore represents, at constant conversions, a more economical mode of operation than purely fluidized-bed operation (1). Compared to purely fixed-bed operation (2), higher conversions are achieved.

I declare, that all statements made in this declaration of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that wilful false statements and the like so made are punishable by fine or imprisonment or both under Section 1001 of Title 18 of the United States Code and that such wilful false statements may jeopardize the validity of the application or any patent issuing thereon.

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